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Air Brush Fabricated Carbon Nanotube Supercapacitor Electrodes

by Matthew H. Ervin and Benjamin S. Miller

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14. ABSTRACT

Carbon nanotube (CNT) films have a high surface area, as well as outstanding physical and chemical stability. When used in creating a supercapacitor electrode, CNTs can result in increased specific capacitance and a lower electrode resistance relative to commercial activated carbon electrodes. The result will be a supercapacitor with increased energy and power density, making supercapacitors better suited for a variety of Army specific applications. This paper reports on the design, fabrication, and testing of supercapacitor electrodes made from single-walled carbon nanotubes (SWCNT), where the CNTs were deposited on the substrate using a spray deposition technique. The CNTs were suspended in acetone or water prior to being sprayed onto the substrate with an airbrush. Other factors are analyzed in the report, including which electrolyte to use as well as the most effective method for spraying the SWCNTs onto a conductive substrate.

15. SUBJECT TERMS

Carbon nanotube, CNT, supercapacitor, air brush

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1. Introduction and Background

In order for the batteries used by Soldiers to provide peak power, an increase in battery size and weight is necessary, which is becoming a burden. A light, compact alternative to large batteries for supplying peak power are electrochemical double layer capacitors. An electrochemical double layer capacitor, or supercapacitor, has a much higher energy density than conventional capacitors. Supercapacitors also have a higher cycle life, higher efficiencies, and a higher specific power than conventional batteries (Pandolfo, 2006). Such supercapacitors will complement batteries and fuel cells to produce hybrid systems with extended capabilities. A review of the literature has shown that commercially available activated carbon supercapacitors using aqueous electrolyte exhibit a specific capacitance of 33 F/g, a specific energy of 13 Wh/kg, and a specific power of 0.58 kW/kg (Obreja, 2008). We ultimately aim to improve on these values by using the exceptional properties of carbon nanotubes to produce electrodes with increased accessible surface area and conductivity, which will result in improved energy and power densities. To fabricate these electrodes, we have focused on a spray deposition technique called airbrushing (Zhao, 2009; Kaempgen, 2009). A spray deposition technique for preparing carbon nanotube (CNT) films over a large area is ideal due to low costs, ease of use, and manufacturability. Other ways to prepare CNT electrodes include vacuum filtration, ink jet printing, dip coating, and electrostatic spray deposition. (Chou, 2008; Lee, 2009; Kim, 2006; Hu, 2009)

2. Motivation

The purpose of this research is to develop an electrode fabrication process that will optimize the CNT electrode capacitance. The main goal is to achieve a specific capacitance in excess of 120 F/g, which is the maximum achievable with activated carbon, the current industry standard (Istvan 2009). This research on CNT supercapacitors will eventually allow Army Soldiers to achieve peak power without having to carry as large a battery.

3. Experiment and Calculations

The nanotubes used for spraying were either pristine single-walled carbon nanotubes (SWCNTs) or carboxylic acid functionalized SWCNTs suspended in acetone or water, with or without the aid of surfactants/dispersants. The CNT solutions were commercially obtained from NanoLab, Inc. and Brewer Science, Inc.

Three different types of SWCNT solution pretreatments were used before the spray deposition. Some of the nanotube solutions were sonicated using a probe sonicator for 2 min at 20% amplitude and then centrifuged for 8 min at 10,000 RPM; some of the SWCNT solutions were only sonicated; and others were used as received. Sonication was used in the hope of debundling the CNTs, and centrifugation was used in an attempt to remove remaining CNT bundles so as to increase the percentage of single tubes.

The substrates used for spray deposition were initially strips of aluminum (Al) foil approximately 1×8.5 cm. The Al foil strip was chosen because of its ease of use and ability to withstand high temperatures. Later experiments used nickel (Ni) foil substrates (current collectors), as they work well with a potassium hydroxide (KOH) electrolyte. During CNT spray deposition, the substrate sat on a hot plate at a temperature of 60–65 ˚C for the initial experiments in which we used acetone-based CNT solutions. We used higher temperatures (175–200 ˚C) in subsequent experiments to speed the evaporation of acetone- and water-based solutions. A circular copper (Cu) weight was placed directly on top of the substrate to prevent movement. The SWCNTs were sprayed at a constant pressure of 6–8 psi. Figure 1 shows this spray deposition apparatus.
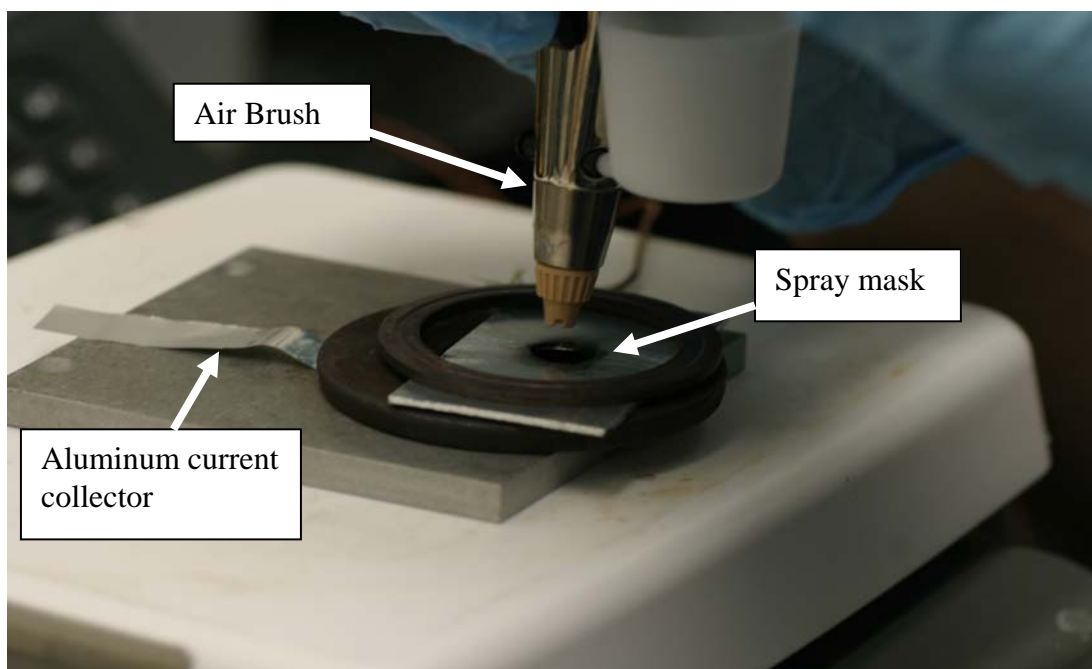
Figure 1. Spray deposition apparatus. The foil substrate is securely placed on a hot plate at a constant temperature. A circular stencil is sometimes used to help define the airbrush deposit.

The type of spray nozzle used on the airbrush was determined by the area we intended to cover and the need for low pressure spraying to prevent splatter. The nozzle that we sprayed with produced a very fine mist at a relatively low pressure range.

A scanning electron microscope (SEM) and an environmental scanning electron microscope (ESEM) were used to image the deposited SWCNT films.

The weight of the deposited SWCNTs was obtained using a microbalance. But for calculating the specific capacitances, the estimated weight of CNTs from the solution volumes is used as the associated mass of surfactant/dispersant is not contributing to the capacitance. The electrochemical, cyclic voltametry, measurements were made using a Keithley 4200 Semiconductor Characterization System or a Princeton Applied Research (PAR) Potentiostat in a three electrode set up. As seen in figure 2, the SWCNT film electrode was used as the working electrode, either a Cu, Ni, or Al foil strip was used as the counter electrode, and a silver/silver chloride (Ag/AgCl) electrode was used as the reference electrode. The electrolytes used were 4 M HNO_3 (1:3 conc. HNO_3:$H2O$, pH=1), dilute 9E-6 M HNO_3 that had a pH=4.5 (a pH at which the oxide coating on the aluminum current collector is stable), or 1 M KOH. The latter was used with the Ni current collectors.
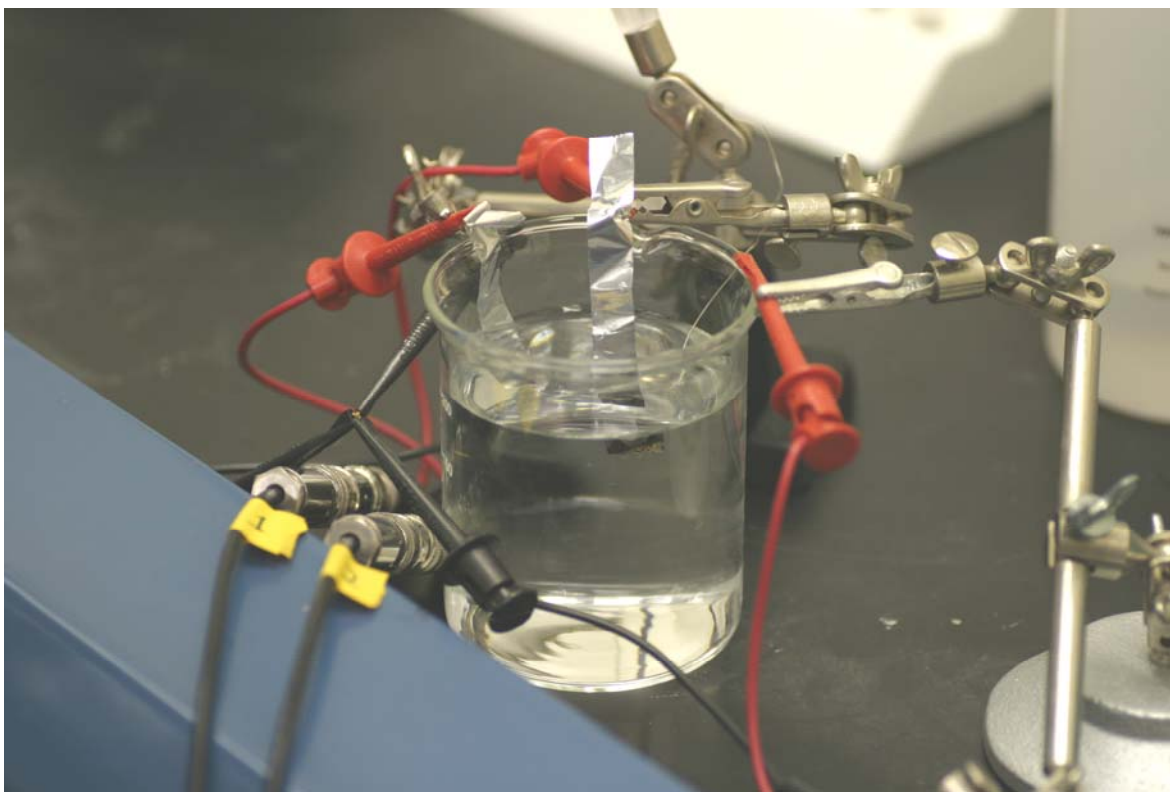

Figure 2. The three electrode cell setup used for CV testing. From left to right: A foil counter electrode, SWCNT working electrode, and Ag/AgCl reference electrode.

The cyclic voltamogram (CV) was performed in potential ranges of anywhere between –0.9–0.5 V at scan rates ranging from 1–100 mV/s. Equation 1 was used to calculate the capacitance of the working electrode:

$$\text{Capacitance} = \text{current} / \text{scan rate} \qquad (1)$$

The capacitance is in F, the current is in amps, and the CV scan rate is measured in V/s. The current is anywhere from mA to nA measured from the CV. In particular, the current is measured from the reductive side of the CV loop at the open circuit potential, where reduction and oxidation (redox) reactions, if present, are in equilibrium. This avoids including redox reaction contributions in the calculation of the double-layer capacitance. If the deduction side of the CV curve is not below zero amps, then half the difference between the oxidative and reductive sides of the CV loop at the open circuit potential is measured and used to calculate the capacitance. Typically, this approach is not needed when a proper potentiostat is used. The specific capacitance is calculated by dividing the capacitance of the working electrode by the mass of CNTs in the film, as estimated from the concentration and volume of CNT solution used. (These specific capacitances are not directly comparable to those for commercial capacitors, since those include the mass of the entire device including the packaging, electrolyte, etc.)

4. Results and Discussion

Table 1 shows how the NanoLab SWCNTs solutions were prepared before being deposited onto Al foil substrates. Spray deposition of the SWCNT suspensions took 5–10 min and covered a ~1 cm^2 area. A SWCNT film deposit is shown in figure 3. During spraying, the acetone would evaporate on contact as long as there wasn't too much liquid on the substrate. If the liquid began to bead on the substrate, the acetone would sit for a few seconds before evaporating. We heated the substrate to a higher temperature in subsequent experiments to speed the evaporation. Increasing the size of the spray area could be favorable in achieving a more uniform evaporation, in that the air brush could be in constant motion, preventing the acetone from beading up as with a stationary deposition. By avoiding large liquid accumulation on the surface, it is hoped that bundling of the CNTs will be kinetically minimized during the drying process. This may help maximize the ultimate surface area and, therefore, capacitance.

Table 1. The type of SWCNTs deposited on each electrode as well as the film mass which includes the mass of CNTs and any surfactant/dispersants in the deposit.

Electrode	CNT functionalization	Sonicated	Centrifuged	CNT film Mass (mg)	Volume Sprayed (mL)
1	Pristine	Yes	Yes	1.4	4
2	Pristine	Yes	No	1.06	1
3	Pristine	No	No	1.16	1
4	None-blank	No	No	0	0
5	Pristine	Yes	Yes	1.92	3
6	Pristine	Yes	No	1.16	1
7	Pristine	No	No	0.74	1
8	Carboxylic	No	No	0.35	1

Figure 3. SWCNT film deposit on Al foil electrode 5.

Figure 4 shows a comparison of a sonicated and centrifuged (#5) SEM image to a non-sonicated (#3) SEM image. The sonicated and centrifuged SWCNT film had the higher mass even though there seemed to be less SWCNTs on the substrate shown in SEM images, as well as capacitance readings. Because there is more mass present in the centrifuged electrode film, but not as many

SWCNTs, it leads to the conclusion that there is a lot more contamination deposited on this film than expected. Presumably, the centrifugation removed the CNTs (CNT bundles) more effectively than the contaminants (surfactants/dispersants).

The surface morphology of the spray-deposited CNT films can be seen in figures 4 and 5. Although the SWCNTs are well-entangled and interconnected, they are not as dense as we had initially hoped for them to be. There also does not seem to be a difference between the sonicated and non-sonicated electrodes in SEM images. There is a lot of contamination present that seems to be clogging the pores expected in these films, decreasing capacitance. The solutions that these CNT films were made from used dispersants and surfactants to aid the solubilization of the CNTs, but which contaminate the final films.
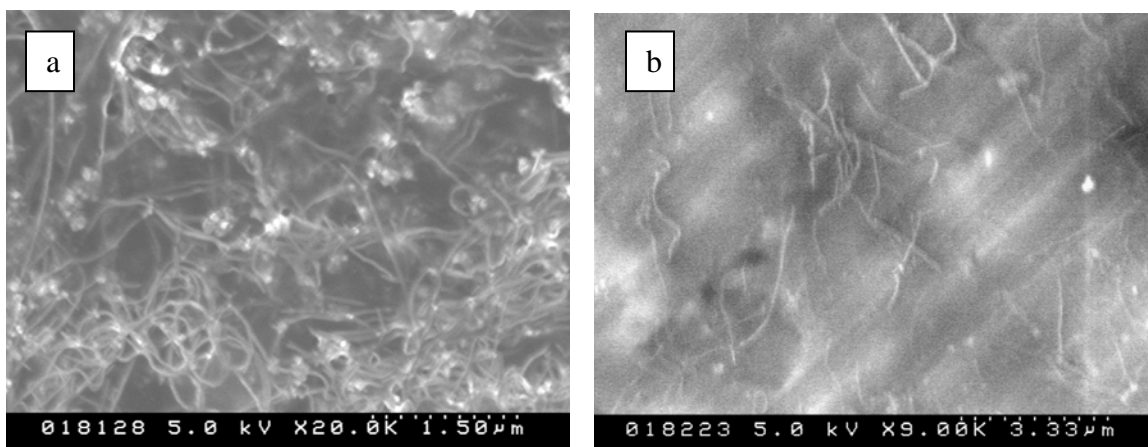
Figure 4. SEM images of SWCNT films on Al foil substrate: (a) electrode 3 non-sonicated SWCNT film and (b) electrode 5 sonicated and centrifuged SWCNT film. Electrode 3 shows a more densely packed surface than that on electrode 5 even though electrode 5's film mass was over 50 % more than that of electrode 3's film mass.
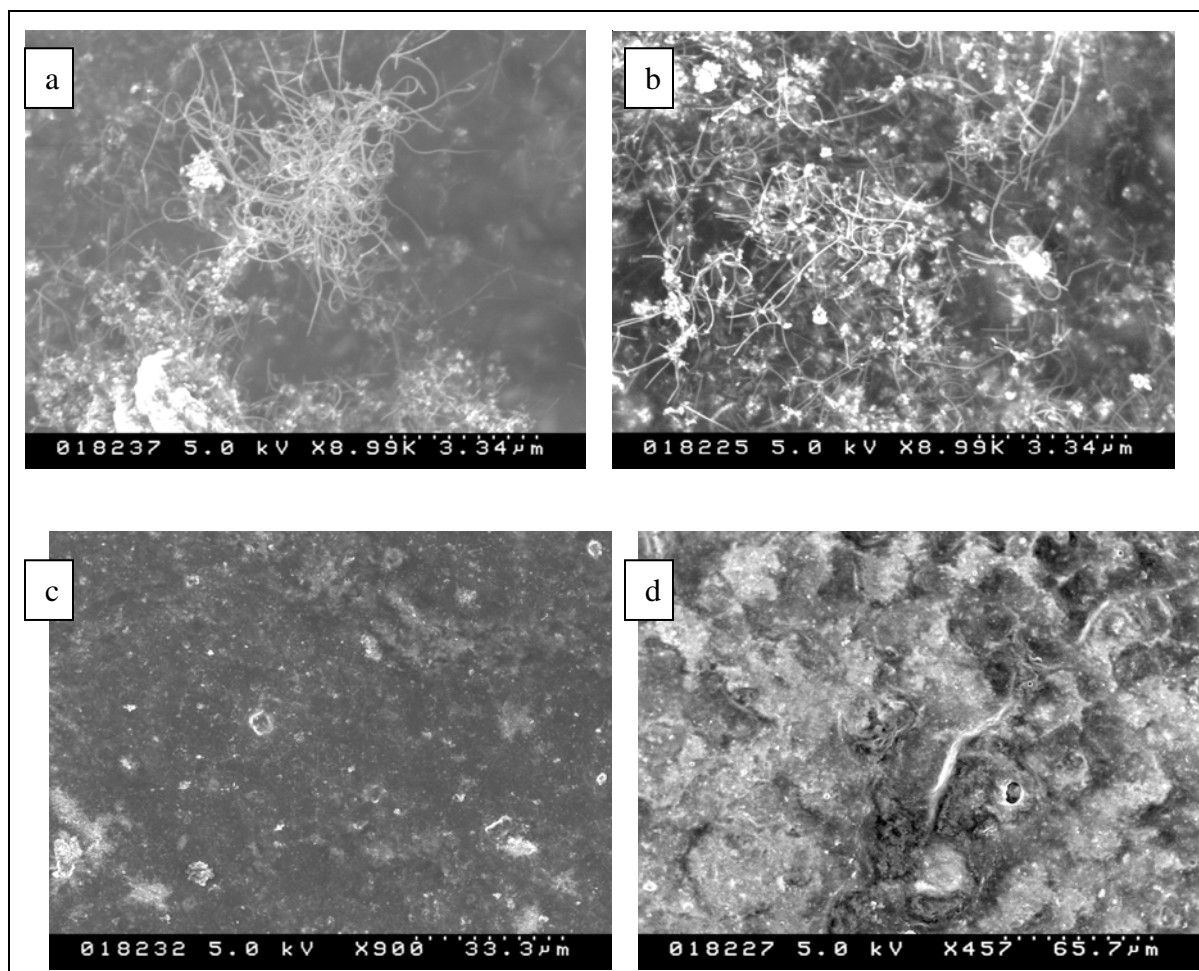
Figure 5. SEM images of SWCNT films on Al foil substrate: (a) electrode 7 non-sonicated SWCNT film zoomed in, (b) electrode 6 sonicated SWCNT film zoomed in, (c) electrode 7 non-sonicated SWCNT film zoomed out and (d) electrode 6 sonicated SWCNT film zoomed out. There is a lot of contamination present.

A few methods were used to clean the electrodes, but none worked well. Soaking electrode 8 in toluene, acetone, and isopropyl alcohol (IPA) did not seem to get rid of the contamination. ESEM images taken before and after the cleaning were nearly identical. Annealing the electrode to approximately 300 °C in hydrogen also did not clean the film. A post-clean attempt on electrode 8 can be seen in figure 6. There seems to be a film covering all of the SWCNTs.
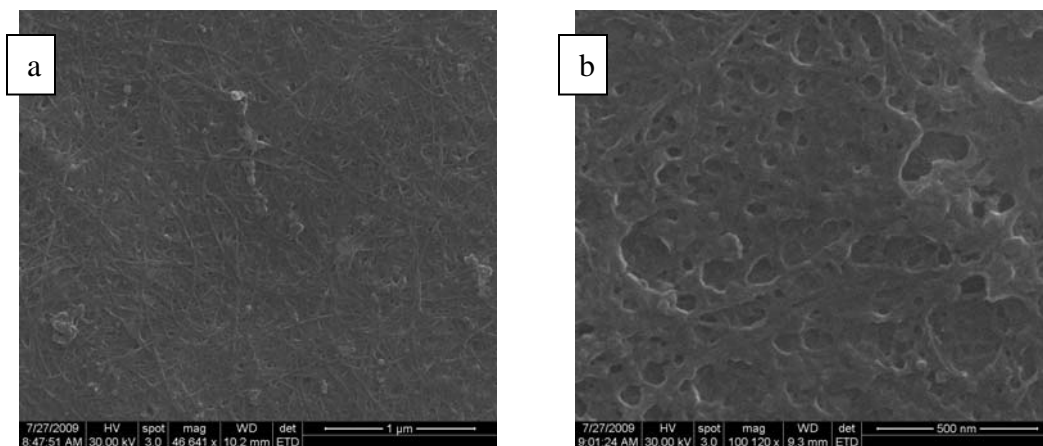
Figure 6. ESEM images on electrode 8 after attempted cleaning: (a) 1 micron scale and (b) 500 nm scale.

The CVs of some of the SWCNT electrodes are shown in figure 7. For all of the films, the specific capacitance will decrease as the scan rate increases because of kinetic limitations of the ion diffusion into the pores of the entangled SWCNTs. There were two different types of HNO_3 electrolytes used during the CV tests in figure 7 and table 2. One of the electrolytes was diluted 1:3 with de-ionized water, while the other was diluted 1:450,000 with de-ionized water.
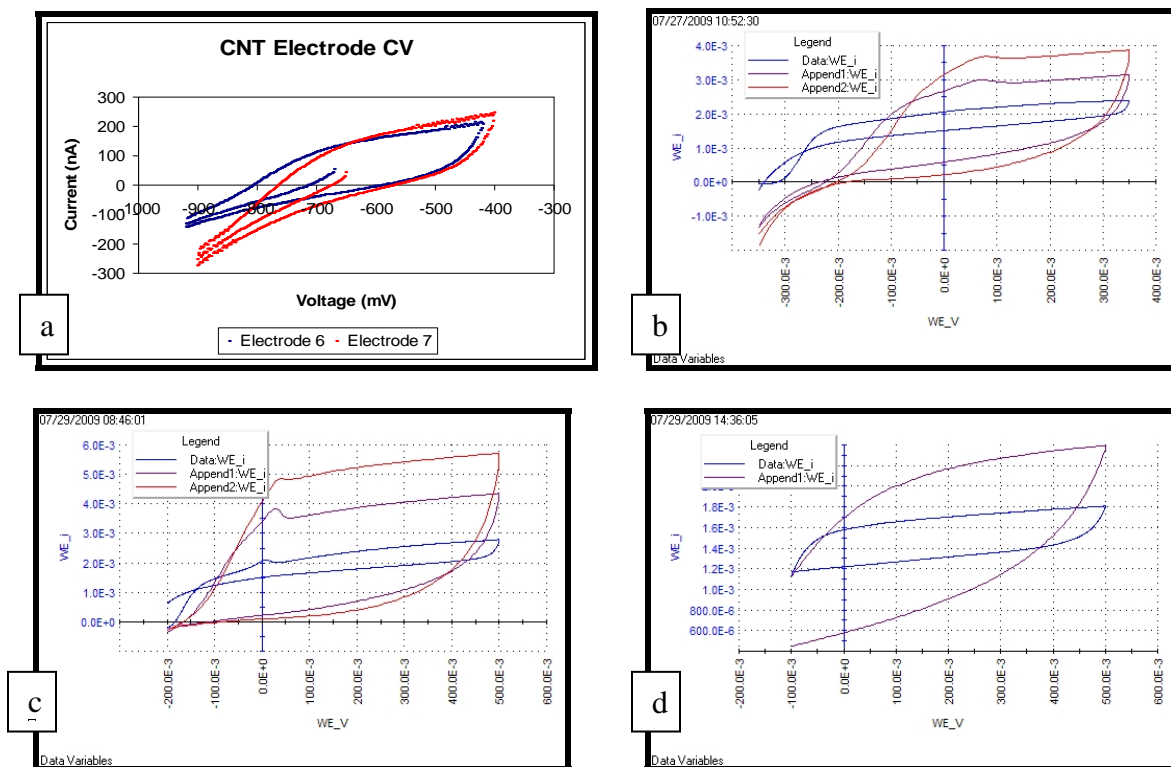
Figure 7. CV readings of the working electrode using the Keithley 4200 or the PAR Potentiostat: (a) Electrode 6 & 7 measured on Princeton Potentiostat at a scan rate of 5 mV/s, (b) Keithley 4200 measurement of electrode 3 at scan rates of 10, 50, and 100 mV/s, (c) Keithley 4200 measurements of electrode 4 (Al blank) at scan rates of 10, 50, and 100 mV/s and (d) Keithley 4200 measurements of electrode 2 at a 10 and 100 mV/s scan rate.

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Table 2. Capacitance results for NanoLab solutions using CNT solutions in acetone using surfactants/dispersants.

Electrode	Scan Rate (mV/s)	Electrolyte	Capacitance	Specific Capacitance (F/g)
6	5	Dilute		.014
7	5	Dilute		.016
3	10	Concentrated	30mF	22
3	50	Concentrated		17
3	100	Concentrated		13
4	10	Concentrated	25mF	N/A (no SWCNT)
4	50	Concentrated	32mF	N/A (no SWCNT)
4	100	Concentrated	23mF	N/A (no SWCNT)
2	10	Concentrated	20mF	19
2	100	Concentrated		6

We found that when making CV tests of the SWCNT electrodes in a higher concentration HNO_3 electrolyte, the film will eventually slip off of the substrate, ruining the electrode, which happened with electrode #8. The high concentration of HNO_3 was etching the aluminum oxide under the SWCNT film, causing it to detach. The SWCNTs, though, did not seem to be detaching from each other. The shape of the CNT film remained intact when floating in the HNO_3. When the electrodes were left overnight in the dilute electrolyte solution, we found that the SWCNT film remained intact on the Al foil substrate.

Figure 7 (a) contains CV curves of electrodes #6 and 7 taken on the Princeton Potentiostat in the dilute HNO_3 electrolyte. The specific capacitance found while performing CV curves in the dilute electrolyte was over 1000 times less than the specific capacitance found while testing in the concentrated electrolyte (e.g., figure 7b). This indicates that the dilute electrolyte is not suitable for making these measurements. As a result, more experiments were performed using a 1 M KOH electrolyte and Ni current collectors, which are more typical materials for such experiments. Electrode 3, shown in figure 7b, was tested using the Keithley 4200 with a much more concentrated solution, and showed significantly higher capacitance. However, when a blank current collector is tested, it can be seen to have similar capacitance (figure 7c), so that the CNT film in electrode #3 does not appear to be contributing much if any capacitance. Similarly, the capacitive current measured for electrode #2 (figure 7d) is also similar to the blank. We believe that the poor capacitance of these CNT films is due to the contamination in these CNT films.

In an attempt to improve the CNT electrode capacitance above that of a blank current collector, we purchased a CNT solution that does not include surfactants or dispersants from Brewer Science, Inc. This solution was tested along side of the NanoLab CNT in acetone with surfactant solutions used previously. Figure 8 shows SEM images of electrodes 9 and 11–13. In figure 8a, the "clean" Brewer Science solution is shown to produce a film with small pores and small CNT bundles. The carboxylated CNT solution that includes dispersant produces a porous electrode, as well, although the CNT bundles look larger due to associated contamination. The remaining two images show that the electrodes made with surfactants/dispersant or aminopyrene are so contaminated with these additives that the films are not porous and appear to charge in the SEM. These additives may be reducing capacitance by reducing the electrode surface area (no pores) by increasing the distance of approach between the electrolyte ions and the CNTs, as well as by increasing the electrode resistance by preventing the CNTs from making good electrical contact between themselves and the current collector.
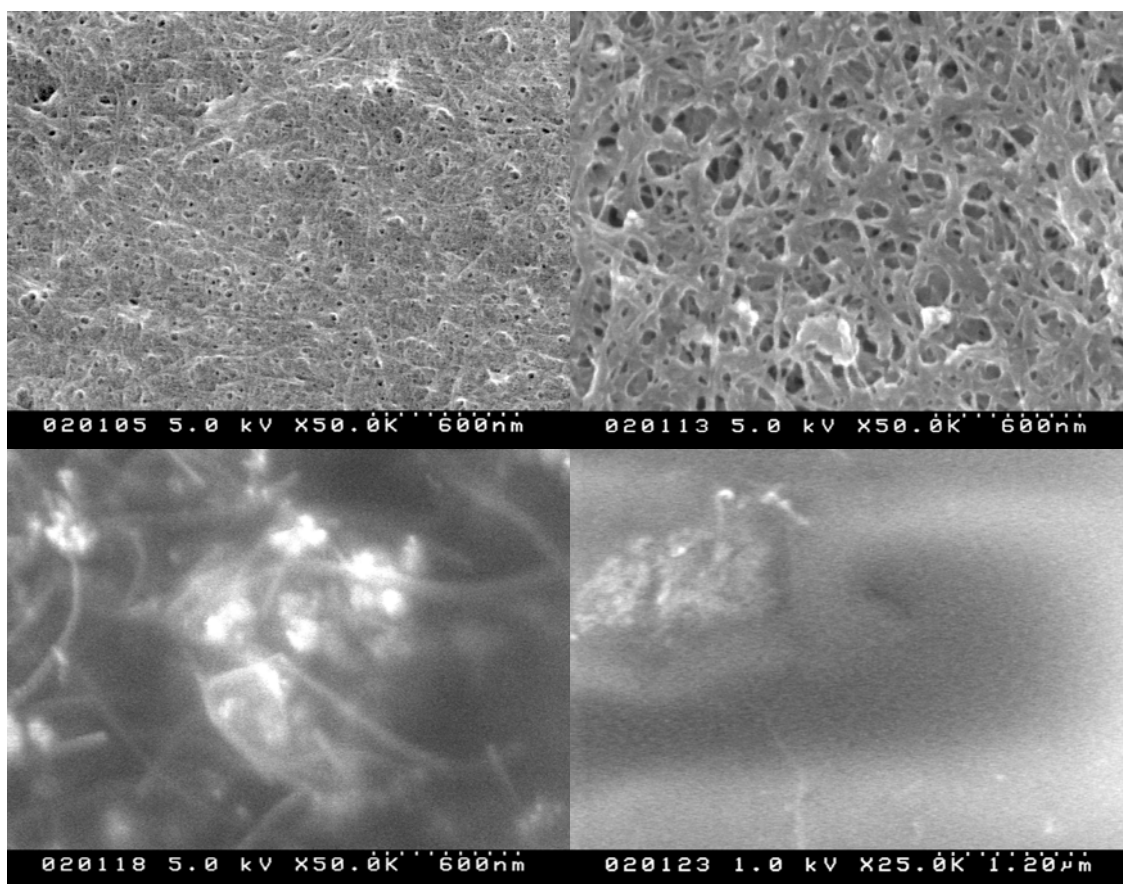

Figure 8. Similar SEM images of SWCNT films on Ni foil current collectors made from: (a) carboxylated CNTs in water with no additives (electrode 9), (b) carboxylated CNTs in acetone with dispersant (electrode 10), (c) pristine CNTs in acetone with surfactant (electrode 11) and (d) CNTs solubilized in acetone using aminopyrene (electrode 12).

CV testing of electrodes 9–14 yields the capacitance results shown in table 3. Electrode 14 is a Ni current collector without any CNTs, which is used as a blank sample to measure the capacitance due to the Ni current collector. This capacitance is subtracted from each electrode's measured total capacitance to obtain a capacitance representative of the CNT's contribution alone. These corrected capacitances are divided by the estimated CNT masses, resultant from the CNT concentrations of the solutions, to obtain the reported specific capacitances. Not surprisingly, electrodes 12 and 13, which appeared nonporous and somewhat electrically insulating in the SEM, yielded little or no increase in capacitance due to the CNT deposits. Electrodes 10 and 11 made with the dispersant containing CNT solution had somewhat better capacitance, presumably due to the increased surface area caused by the porosity of the deposit. The clean deposit obtained using the surfactant/dispersant-free solution yielded the best specific capacitance of all. This could be due to a range of factors including the porosity, small CNT bundles, and the cleanliness of the CNTs in the electrode, which allows the electrolyte ions to approach close to the CNTs. In a traditional capacitor, the capacitance is proportional to the overlapping area of the electrodes and inversely proportional to the gap between the electrodes (the dielectric thickness). A properly made supercapacitor is able to store so much energy in part because the ions can adsorb within a few atomic distances of the CNT electrode.

Table 3. Comparison of different CNT solutions for making electrodes.

Electrode	CNT solution	Surfactant Or Dispersant?	CNT solution volume (ml)	CNT mass (µg)	Total Capacitance (mF)	Specific Capacitance (F/g)
9	Brewer Sci – carboxylic	N	1	50	2.9	53
10	NanoLab - carboxylic	Y	0.5	200	0.55	1.5
11	NanoLab - carboxylic	Y	0.25	100	0.8	5.5
12	NanoLab - pristine	Y	0.25	100	0.25	—
13	NanoLab - aminopyrene	Y	0.25	100	0.19	—
14	None (blank)	N/A	0	0	0.25	—

5. Summary and Conclusions

Part of this work consisted of developing the electrode fabrication and testing protocols for investigating CNT-based supercapacitor electrodes. Our initial results showed that using Al current collectors with a nitric acid electrolyte was not a viable system. While the Al current collector electrodes were stable in dilute nitric acid, the measured capacitances were low, presumably due to electrolyte resistance. At higher concentration, the electrodes were no longer

stable. After switching to Ni current collectors and KOH electrolyte, our electrodes were stable and yielded useful capacitance data. A comparison of electrodes formed by airbrush deposition of various commercial CNT solutions yielded a wide range of specific capacitances. In particular, solutions that used surfactants and/or dispersants produced poor specific capacitances due to contamination of the CNTs, yielding poor porosity and conductivity. Electrodes made a solution of carboxylated CNTs and water only produced the cleanest looking electrodes and the largest specific capacitance of 53 F/g. Further experiments are underway to determine what role the fabrication process, itself, has on the specific capacitance achieved.

6. References

Pandolfo, A. G.; Hollenkamp. A. F. *J. Power Sources* **2006**, *157*, 11–27.

Zhao, X.; et al. *Nanotech* **2009**, *20*, 065605.

Kaempgen, M.; Chan, C. K.; Ma, J.; Cui, Y.; Gruner, G. *Nano Lett* **2009**, *9*, 1872–1876.

Lee, S. W.; Kim, B.-S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. *J. Amer. Chem. Soc.* **2009**, *131*, 671–679 (2009).

Chou, S.-L.; Wanga, J.-Z.; Chew, S.-Y.; Lui, H.-K.; Dou, S.-X. *Electrochem. Comm.* **2008**, *10*, 1724–1727.

Kim, J. H.; Nam, K.-W.; Ma, S. B.; Kim, K. B. *Carbon* **2006**, *44*, 1963–1968.

Hu, L.; Choi, J. W.; Yang, Y.; Jeong, S.; La Mantia, F.; Cui, L.-F.; Cui, Y. *Proc. Nat. Acad. Sci.* **2009**, *106*, 21490–21494.

Isvan, R.   The 19th Int'l Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Deerfield Beach, FL 7–9 Dec 2009.

Obreja, V.V.N., *Physica E.* **2008**, *40*, 2596–2605.

List of Symbols, Acronyms, and Abbreviations

AL   aluminum

CNT   carbon nanotube

Cu   copper

CV   cyclic voltamogram

ESEM   environmental scanning electron microscope

F/g   Farads per gram

IPA   isopropyl alcohol

KOH   potassium hydroxide

mF   milliFarad

mg   milligram

ml   milliliter

Ni   nickel

PAR   Princeton Applied Research

SEM   scanning electron microscope

SWCNT   single wall carbon nanotube

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